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Material properties

Mechanical properties and morphology of NBR with different clays

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ABSTRACT

Nanocomposites of NBR with different types of clays were prepared and characterized in terms of their morphology by X-ray diffraction and mechanical properties. It was observed that the organo-modifier agent of the clays and the molar mass of rubber had a significant influence on the dispersion of the clay lamellae during mixing on a two-roll mill. The results suggest that this simple and quick method of mixing and compounding seems to be viable to obtain reinforced materials on the nanoscale.

1. Introduction

Nowadays, nanocomposites are among the most studied materials. There are several reasons for this enthusiasm in the scientific community, especially due to the fact that even small amount of filler can promote significant enhancement on some properties of the matrix, such as mechanical ones, to a level several times their original values [1–5]. These improvements are remarkable when in comparison to the properties of both pure polymer and when prepared in the form of microcomposites [6]. Among the fillers used in nanocomposites, montmorillonite, which belongs to the general family of 2:1 layered or phyllosilicates, can be mentioned as the most studied [5,7].

Depending on the nature of the components (clay, organic cation and polymer matrix) and the method of preparation used, three main types of composites can be obtained when layered clay is associated with a polymer: a microcomposite, an intercalated nanocomposite and an exfoliated nanocomposite [3,8,9].

X-ray diffractometry is often used to identify intercalated structures, due to its capacity to investigate order on the nanoscale level. Despite the higher separation between the lamellae in such nanocomposites, the repetitive multilayer structure is well preserved, and the interlayer can be determined. The intercalation of the polymer chains, which is responsible for the increase in the interlayer spacing, leads to a shift in the diffraction peak towards lower angles (angle and layer spacing are related through Bragg's Law: $\lambda = 2.d.\sin\theta$, where λ corresponds to the wave length of the X-ray, d is the spacing between diffractional lattice planes and θ is the measured diffraction angle or glancing angle) [8].

When organomodified clay is incorporated into the polymer, the improvement observed in some properties is due to the restrictions on the mobility of the polymer chains around the clay particle [10]. Thus, these improvements depend on the dispersion level, the degree of delamination, the form factor of the clay, and the interfacial interactions between polymer and clay. Some of these properties are improved only if these structures are completely exfoliated, that is, lose their stacking order, enabling effective transfer of stresses and increasing the reinforcing effect [11].

Some authors have reported variations in the mechanical properties of rubber such as NR [3,9,12–16], NBR [17], SBR [14,17], BR [14], ENR [6] and EPDM [14] by choosing the type, the amount and the organic modification of the clay [3,9,11,12,15,18–30].

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Table 1
Recipes of the rubber compounds.

Compound	Amount (phr)
NBR	100
Struktol WB-220® (plasticizer)	5
Flectol TMQ® (antioxidant)	1
Zinc oxide	5
Stearic acid	2
MBTS (acelerator)	1,5
TMTD (acelerator)	0,5
Sulphur	1,5
Clay	0, 1, 3, 5 and 7

Table 2
Sample codes used in this article.

Nanofiller	Amount (phr)	Sample Code (NBR 3330)	Sample Code (NBR 3350)
		N30-0	N50-0
Bentonite	1	N30-B1	N50-B1
	3	N30-B3	N50-B3
	5	N30-B5	N50-B5
	7	N30-B7	N50-B7
Cloisite 30B®	1	N30-30B1	N50-30B1
	3	N30-30B3	N50-30B3
	5	N30-30B5	N50-30B5
	7	N30-30B7	N50-30B7
Cloisite $Na^{+®}$	1	N30-Na⁺1	N50-Na⁺1
	3	N30-Na⁺3	N50-Na⁺3
	5	N30-Na⁺5	N50-Na⁺5
	7	N30-Na⁺7	N50-Na⁺7

In this work, mechanical properties of nanocomposites NBR with different clays were measured and the results are compared to their X-ray diffraction patterns. One important point is that the difference between Mooney viscosity of NBR and, consequently, its molecular weight, had a significant influence on the dispersion level of the clay lamellae in the nanocomposites.

2. Experimental

2.1. Materials

Two grades of NBR were kindly donated by Petroflex S/A under the trade names NBR 3330 (Mooney viscosity, ML(1 + 4) 100 °C 28) and NBR 3350 (Mooney viscosity, ML(1 + 4) 100 °C 48), both with 33% bound acrylonitrile. Different clays were used in the formulations: Sodic montmorillonite, Cloisite $Na^{+®}$, organophilic modified montmorillonite Cloisite 30B® (both produced by Southerm Clay Inc), and a Brazilian clay, Bentonite (produced by Bentonit União).

2.2. NBR nanocomposites preparation

Rubber compounds were prepared on a two-roll mill at room temperature. The rolls operated at a speed ratio of 1:1.4. The vulcanization additives (conventional cure system) were added to the elastomer prior to the incorporation of the filler. The recipes used in this work are described in Table 1. Vulcanization conditions (temperature and time) were previously determined using a Monsanto moving die rheometer Alpha Technologies Model MDR 2000. Rubber compounds were vulcanized at 160 °C and pressure of 45 Kgf/cm^2 in a hydraulic press. The vulcanization time of the sheets corresponds to optimum cure time (t_{90}) derived from the curing curves of the MDR 2000. The value of t_{90} found was 3,18 min, which was extrapolated to 4 min to ensure that all samples were totally vulcanized. Vulcanized material was then cut into dumbbell shaped tensile test according to ASTM D412, type IV. The sample codes used in this article are showed in Table 2.

2.3. Characterization

The tensile properties of the vulcanizates were evaluated on an Instron Universal Test Machine Model 4202, according to ASTM D412. Tensile strength, elongation at

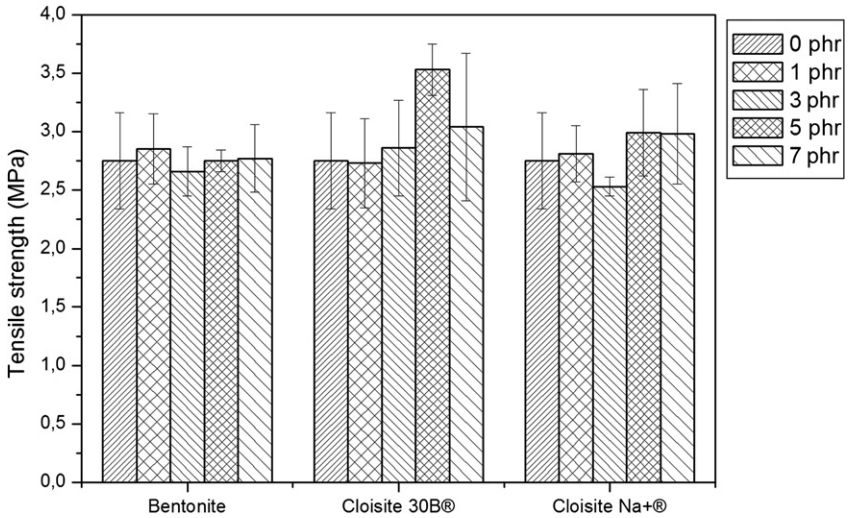

Fig. 1. Tensile strengths of NBR 3330 and nanocomposites with different clays.

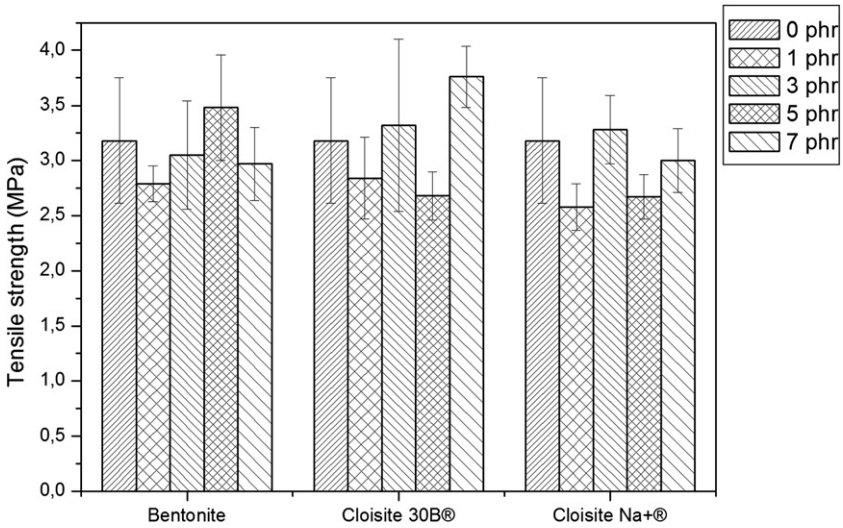

Fig. 2. Tensile strengths of NBR 3350 and nanocomposites with different clays.

break and elastic modulus at 100% elongation were obtained. The rate of grip separation was 500 mm/min.

A Rigaku Model RU 200B diffractometer was used to study the XRD patterns of clay and NBR nanocomposites. Tests were carried out with 2θ scanned from 2° to 10° at 2°/min scanning rate, using Cu Ka ($k = 0.15418$ nm) radiation.

3. Results and discussion

3.1. Mechanical properties

Figs. 1–6 compare the mechanical properties of the nanocomposites based on NBR 3330 and NBR 3350, where the vertical bars represent the standard deviation. In general, NBR 3350 showed better mechanical properties than NBR 3330. This is probably due to the higher mechanical stresses imposed on the material with higher viscosity during the mixing on the two roll mill, forcing the separation of the clay lamellae. Thus, the mechanical stresses act directly on the filler dispersion, changing the dispersion level of the clay lamellae in the nanocomposites.

Regarding the results for the NBR 3330, there were slight improvements in certain properties, as it can be seen especially when Cloisite 30B® and Cloisite Na^{+}® are used. When comparing the elongation at break (Fig. 3) of NBR with 1 phr Bentonite (463%) with neat rubber (236%), a marked increase is observed.

The properties of nanocomposites based on NBR 3350 (Figs. 2,4 and 6), showed noticeable changes when the values are compared to the ones based on NBR 3330. All the

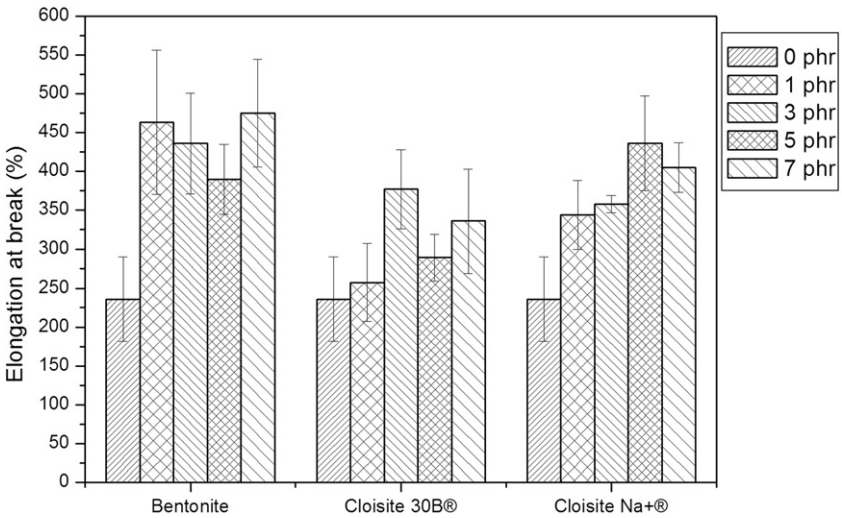

Fig. 3. Elongations at break of NBR 3330 and nanocomposites with different clays.

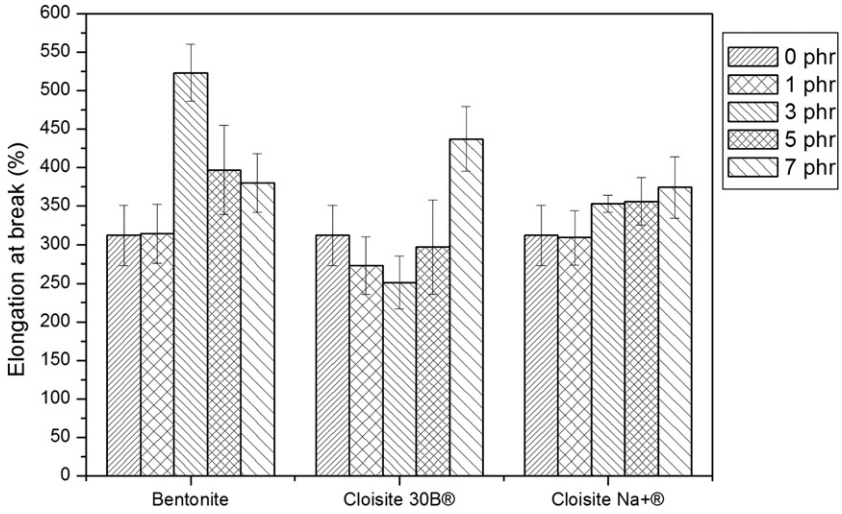

Fig. 4. Elongations at break of NBR 3350 and nanocomposites with different clays.

samples showed an increase in their properties with 3 phr of nanofiller, including Bentonite that showed the highest value of elongation at break (523%).

3.2. Organoclay characterization

Figs. 7–12 show the X-ray patterns obtained from the neat rubber and the nanocomposites NBR/clay.

Regarding the nanocomposites NBR/Bentonite (Figs. 7 and 10), there was evidence of intercalation in both rubbers (NBR 3330 and 3350). However, in the case of NBR 3350 with 7 phr of Bentonite, probably the higher clay content caused poor dispersion in the rubber matrix, with a low level of intercalation in comparison with the other samples.

In the case of nanocomposites NBR/Cloisite 30B® (Figs. 8 and 11), there are no noticeable peaks related to the clay in compositions until 5 phr of clay; this is possibly caused by the complete exfoliation of the clay. With 7 phr of clay, the clay shows some different diffaction peaks, probably caused by different levels of intercalation present in this nanocomposite. A broadening of the peak related to the clay can be seen, suggesting a clay population with lower spacing between the lamellae than the original one.

Comparing the two types of rubber used in the nanocomposites NBR/Cloisite $Na^{+®}$ (Figs. 9 and 12), a slight peak broadening of the sample with NBR 3350 as the matrix suggests a higher level of intercalation. The presence of a new peak at lower values of 'θ' can also be observed, that is, it is possible that intercalation to a specific interlayer spacing is obtained, generating a population of particles ordered with almost the same distance between the lamellae. The peaks generated by the nanocomposites NBR/Cloisite $Na^{+®}$ showed the lowest variation compared to the other materials studied. This is probably due to the low

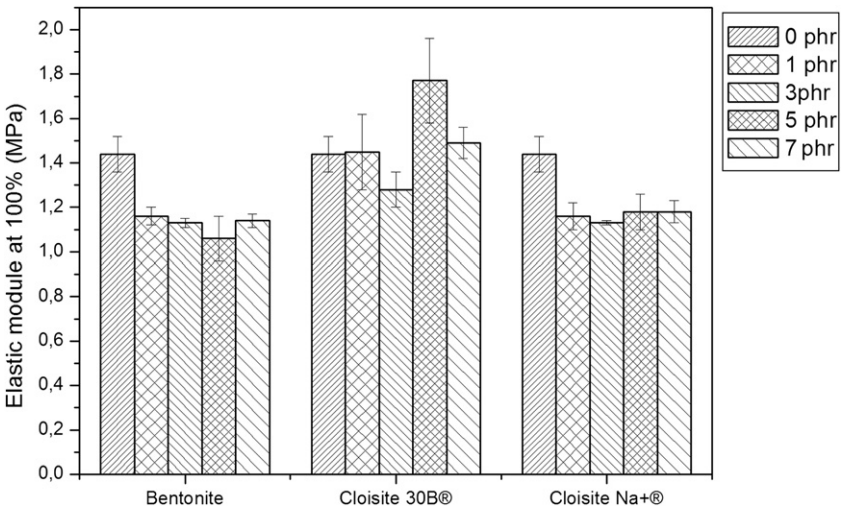

Fig. 5. Elastic modulus at 100% elongation of NBR 3330 and nanocomposites with different clays.

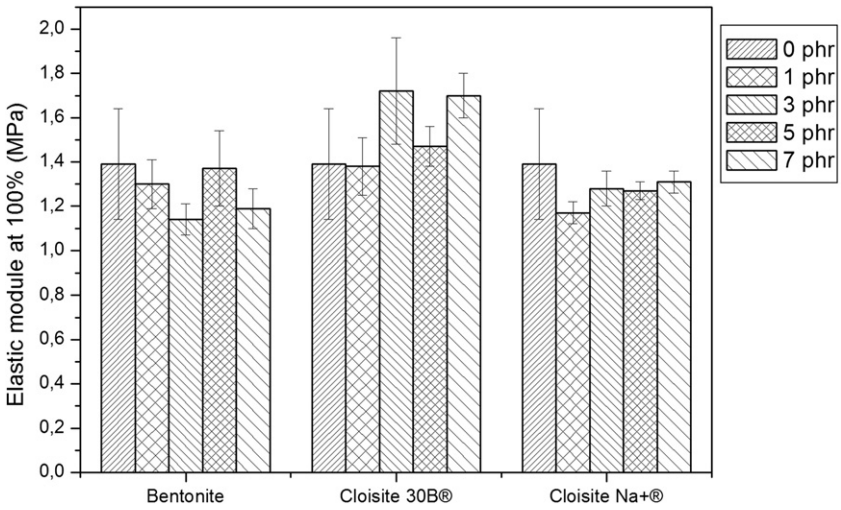

Fig. 6. Elastic modulus at 100% elongation of NBR 3350 and nanocomposites with different clays.

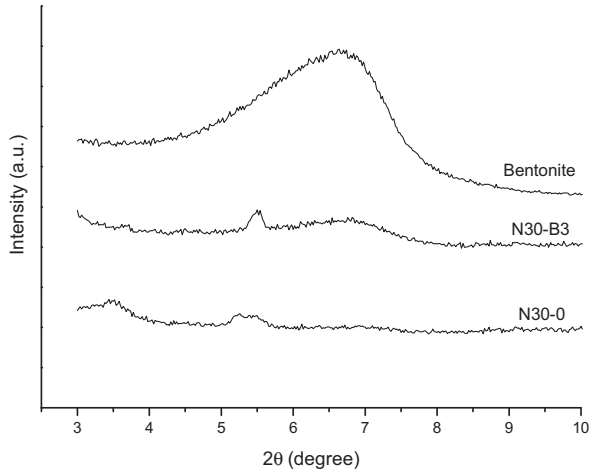

Fig. 7. X-ray patterns of Bentonite, nanocomposite NBR 3330/3phr of Bentonite and neat NBR 3330.

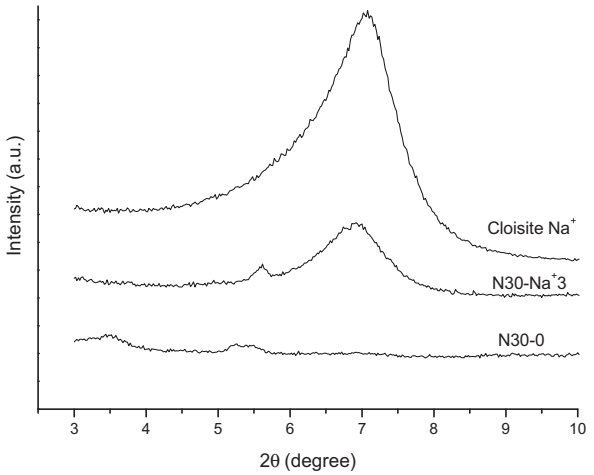

Fig. 9. X-ray patterns of Cloisite $Na^{+®}$, nanocomposite NBR 3330/3phr of Cloisite $Na^{+®}$ and neat NBR 3330.

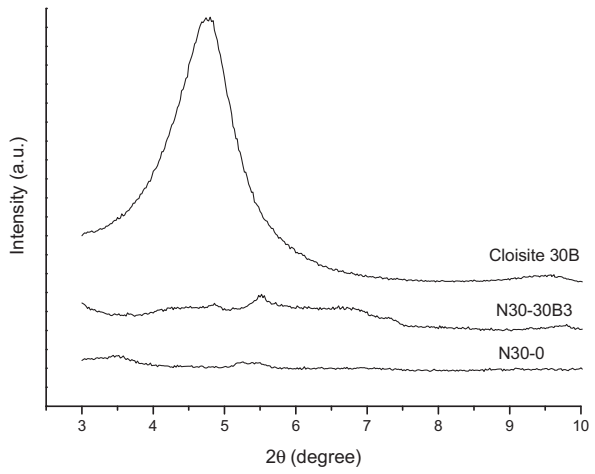

Fig. 8. X-ray patterns of Cloisite 30B®, nanocomposite NBR 3330/3phr of Cloisite 30B® and neat NBR 3330.

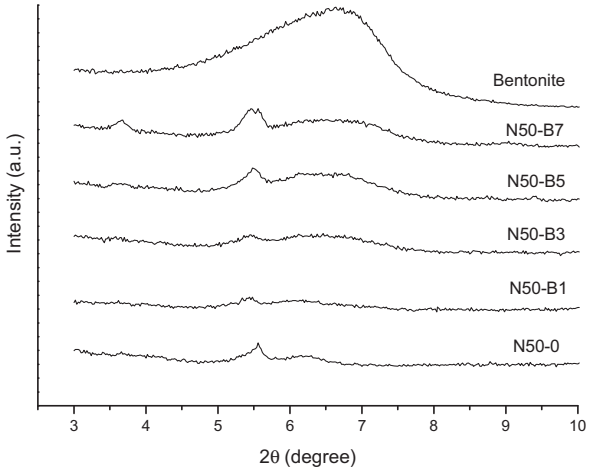

Fig. 10. X-ray patterns of Bentonite and nanocomposites NBR 3350/ Bentonite in different concentrations.

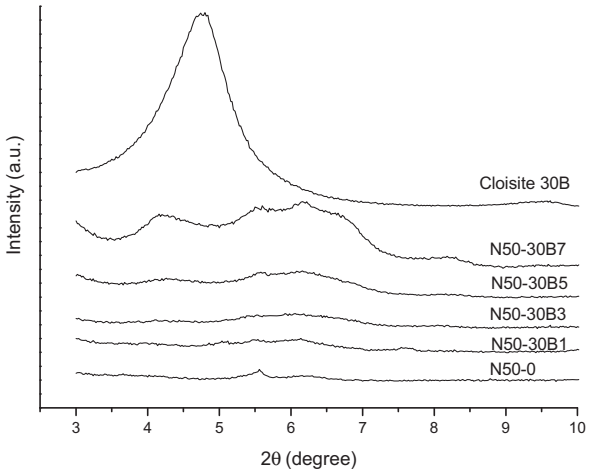

Fig. 11. X-ray patterns of Cloisite 30B® and nanocomposites NBR 3350/ Cloisite 30B® in different concentrations.

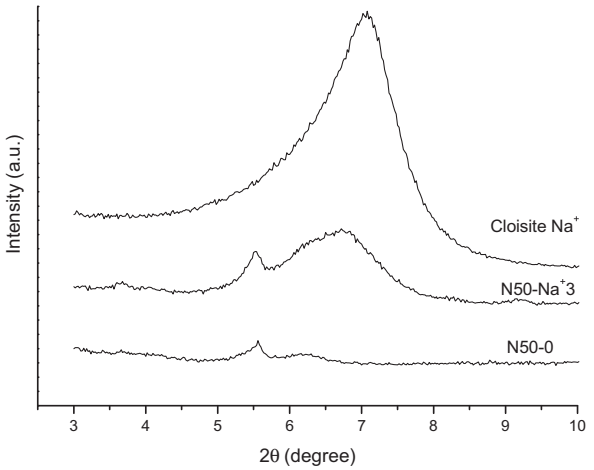

Fig. 12. X-ray patterns of Cloisite Na^{+}®, nanocomposite NBR 3350/3phr of Cloisite Na^{+}® and neat NBR 3350.

interaction between the phases, since the polymer is organic and the clay is hydrophilic.

4. Conclusions

The incorporation of organically modified and unmodified montmorillonites in NBR matrix by open two roll mill mixing shows this to be a viable, simple and quick way to obtain reinforced materials. X-ray diffraction of the samples prepared in this way showed that there was intercalation of the polymeric chains between the clay layers, especially when organically modified clay is used, which caused an increase in mechanical properties when compared to the neat rubber.

The molar mass of the polymer seems to have a significant effect on the intercalated state of the nanocomposite, due to a higher viscosity imposing a higher mechanical stress on the clay during the mixing. This stress acts as a driving force for the intercalation of the polymer molecules between the clay layers. This effect could be seen from the X-ray results.

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References

[1] P.C. Lebaron, et al., Polymer-layered silicate nanocomposites: an overview, Appl. Clay Sci. 15 (1999) 11.
[2] P.M. Ajayan, et al., Nanocomposite Science and Technology. Wiley-VCH Ed. Verlag, 2003.
[3] L. Liu, et al., Structure and properties of Natural Rubber-Organoclay nanocomposites prepared by grafting and intercalating method in latex, J. Elast Plast. 38 (2006) 147.
[4] E. Taghizadeh, et al., Effects of organoclay on the mechanical properties and microstructure of PA6/ECO blend, Polym. Test. 30 (2011) 327.
[5] L. Cauvin, et al., Mechanical properties of polypropylene layered silicate nanocomposites: characterization and micro-macro modeling, Polym. Test. 29 (2010) 245.
[6] N. Mohamad, et al., Correlation of filler loading and Silane coupling agent on the physical characteristics of epoxidized Natural Rubber-Alumina nanoparticles composites, J. Elast Plast. 42 (2010) 331.
[7] S.S. Ray, M. Okamoto, Polymer/layered silicate nanocomposites: a review from preparation to processing, Progr. Polym. Sci. 28 (2003) 1539.
[8] M. Alexandre, P. Dubois, Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials, Mat Sci. Eng. 28 (2000) 1.
[9] A.K. Bowmick, et al., Exfoliation of nanolayer assemblies for improved Natural Rubber properties: methods and theory, J. Elast Plast. 42 (2010) 517.
[10] G. Allegraa, et al., Theories and simulations of polymer-based nanocomposites: from chain statistics to reinforcement, Progr Polym. Sci. 33 (2008) 683.
[11] M. Mondragón, et al., Injection molded thermoplastic starch/natural rubber/clay nanocomposites: morphology and mechanical properties, Carboh Polym. 77 (2009) 80.
[12] M. Arroyo, et al., Organo-montmorillonite as substitute of carbon black in natural rubber compounds, Polymer 44 (2003) 2447.
[13] F. Avalos, et al., Effect of montmorillonite intercalant structure on the cure parameters of natural rubber, Europ Polym. J. 44 (2008) 3108.
[14] Q. Liu, et al., Properties of vulcanized rubber nanocomposites filled with nanokaolin and precipitated silica, Appl. Clay Sci. 42 (2008) 232.
[15] N. Rattanasom, et al., Reinforcement of natural rubber with silica/carbon black hybrid filler, Polym. Test. 26 (2007) 369.
[16] W. Jincheng, et al., Novel reinforcing filler: application to natural rubber (NR) system, J. Elast Plast. 37 (2005) 169.
[17] A. Bandyopadhyay, et al., Synthesis, characterisation and properties of clay and silica based rubber nanocomposites, Mat Sci. Tech. 22 (2006) 818.
[18] Y. Liang, et al., A new strategy to improve the gas barrier property of isobutylene–isoprene rubber/clay nanocomposites, Polym. Test. 27 (2008) 270.
[19] Z. Peng, et al., Self-assembled natural rubber/silica nanocomposites: its preparation and characterization, Comp. Sci. Tech. 67 (2007) 3130.
[20] W. Hwang, et al., Preparation and mechanical properties of nitrile butadiene rubber/silicate nanocomposites, Polymer 45 (2004) 5729.
[21] H. Essawy, D. El-Nashar, The use of montmorillonite as a reinforcing and compatibilizing filler for NBR/SBR rubber blend, Polym. Test. 23 (2004) 803.
[22] H. Ismail, R. Ramli, Organoclay filled natural rubber nanocomposites: the effects of filler loading and mixing method, J. Reinf Plast. Compos 2008 (1909) 27.

[23] Y. Munusamy, et al., Ethylene vinyl acetate/natural rubber/organoclay nanocomposites: effect of sulfur and peroxide vulcanization, J. Reinf Plast. Compos 2008 (1925) 27.
[24] M.A. Kader, et al., Preparation and properties of nitrile rubber/montmorillonite nanocomposites via latex blending, J. Mat. Sci. 41 (2006) 7341.
[25] J.W. Chung, et al., Application of strain-time correspondence as a tool for structural analysis of acrylonitrile-butadiene copolymer nanocomposites with various organoclay loadings, Europ Polym. J. 45 (2009) 79.
[26] F. Delor-Jestin, et al., Thermal ageing of acrylonitrile-butadiene copolymer, Polym. Degrad. Stab 70 (2000) 1.
[27] Z. Gu, et al., Preparation and properties of organo-montmorillonite/cis-1,4-polybutadiene rubber nanocomposites by solution intercalation, Appl. Clay Sci. 45 (2009) 50.
[28] R.N. Hakim, H. Ismail, The comparison of organoclay with respect to silica on properties of natural rubber nanocomposites, J. Reinf. Plast. Compos. 28 (2009) 1417.
[29] N. Rattanasom, et al., Comparison of the mechanical properties at similar hardness level of natural rubber filled with various reinforcing-fillers, Polym. Test. 28 (2009) 8.
[30] H. Zheng, et al., Influence of clay modification on the structure and mechanical properties of EPDM/montmorillonite nanocomposites, Polym. Test. 23 (2004) 217.